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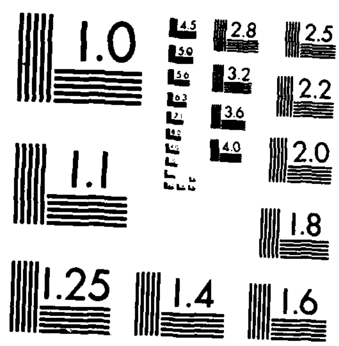

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Cermet coatings are thermal sprayed onto aluminum shipplate to give thermal and fire barrier protection. It is observed that these coatings are highly effective means for effecting such long-term passive protection.

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FINAL REPORT

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Attn: Dr. Homer Carehart
Code 6180

THERMAL BARRIER COATINGS FOR SHIPBOARD PROTECTION

Contract No. N00014-82-K-2063

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THERMAL BARRIER COATINGS FOR SHIPBOARD PROTECTION

The use of aluminum for ship structural members is dictated by design criteria involving strength-to-weight ratios. There are however, significant deficiencies associated with the use of this light metal: a low melting point (659°C) and a high thermal conductivity (2.5 $Wcm^{-1}K^{-1}$). For comparison purposes, mild steel melts at 1427°C and has a thermal conductivity of 0.6 $Wcm^{-1}K^{-1}$. Aluminum melts in fire situations, creating hazards to personnel and equipment. In addition, the heat can seriously degrade the mechanical properties of aluminum alloys even during brief thermal excursions above about 200°C.

It would, therefore, be of considerable advantage to protect the aluminum structure, and this was carried out by thermal spraying of a cermet coating. Oxide coatings are well known as thermal barriers [1] and many investigators have studied their performance when deposited onto superalloy turbine blades. The superalloys have coefficients of thermal expansion (α) from 10 to 19 X $10^{-6}{}^{\circ}C^{-1}$ and it has been found [2] that the low expansion materials (e.g., $\gamma|\gamma - \alpha$ Ni base alloy) exhibit the best thermal cycling lifetimes. In fact, much discussion [3,4] has been generated about the role of expansivity differences between the coating and substrate; and for aluminum this problem will be accentuated by a high α (23 X $10^{-6}{}^{\circ}C^{-1}$).

The main problems addressed in this work are the ability for a cermet coating to perform as a fire barrier. Also of importance will be the corrosion characteristics and mechanical properties of the cermet when attached to the substrate. Thus, there was no requirement for the coating to be subjected to repeated cycling (although this may be a desirable property) since in practice the aluminum structure would be reconditioned. The most important property of the coating is in

de..ying (or preventing) failure of the aluminum substrate. Much attention was also paid to simple manufacture of the coatings and to this end a cermet formulation was developed rather than a duplex or graded coating.

EXPERIMENTS

Thermal Tests

Specimen fabrication was carried out by spraying the premixed powders (0, 20, 40, 80, 100% Al_2O_3 and 0, 40, 50, 60, 70% ZrO_2 with the balance being Ni-Al) with a Metco 5P Thermospray gun (parameters shown in Table 1) onto grit blasted aluminum (alloy 6061 T651) panels (152 X 100 X 9.5 mm = 6 X 4 X 3/8 inches). All of the coatings were laid down to a thickness of 0.25 mm (= 0.010 inches) in order that valid comparisons of the coating conductivities could be made.

A flame test was devised to examine the thermal properties of the coating and substrate. The heat source used as a "standard" flame was chosen for its convenience - i.e., it was the Metco 5P Thermospray gun with 5P7-G nozzle which was held 152 mm (6 inches) from the center of the substrate. As a general comment, it should be noted that a standard flame does not exist in any real situation, and thus the flame used in these tests only allowed the relative conductive properties of the cermet coatings to be established. The substrate was instrumented with two thermocouples which were placed into holes (2 mm diameter and 3 mm deep) drilled into the back of the substrate at positions corresponding to the torch center and 50 mm off-center. Therefore, the temperature *vs* time history of the substrate was recorded to study the insulative effect of the coating on the substrate conductivity.

The above techniques enabled the coatings to be distinguished with respect to their thermal barrier properties. In conjunction with these "quantitative tests" some destructive measurements were also performed. Thus, the panels were subjected to tests where the time for melting of the substrate indicated

its fire susceptibility. The former "non-destructive" tests allowed several measurements so that the reproducibility of the particular test technique could be ascertained.

Corrosion Tests

Salt water immersion tests similar to ASTM standard G34-72 [5] but using a standard salt solution [6] were carried out on the cermet coatings. The initial results were largely negative and it is expedient to discuss and conclude them in this section.

Active corrosion resulted in coating undermining and lift off. The metal alloy portion of the cermet coating, Ni-Al, was formed by cladding one metal with the other, mixing this composite with the oxide, and spraying. Clearly, free aluminum formed within the coating, giving rise to an active electrochemical couple between the free aluminum and nickel. The problem of corrosion was solved by employing a Ni-Al alloy powder atomized from the melt and having no free aluminum. No electrochemical cell developed on placing such a coating within electrolyte.

Mechanical Tests

A major acceptance criterion for the cermet coating, other than its fire barrier capabilities, is its adhesion to the substrate under bending loads. The residual stress at the coating surface (under normal spraying procedures) is tensile [7] so bending tests were designed to maximize this stress and, therefore, the coatings were tested in tension. The substrate dimensions were approximately 15.2 X 2.5 X 0.95 cm (6 X 1 X 3/8 inches), and these were sprayed with cermet coatings of 50 ZrO_2, 40 ZrO_2, 40 Al_2O_3 and 20 Al_2O_3 (in weight percent with the balance being NiAl) to a thickness of 0.5 mm (0.020 inches). The specimens were tested with the coatings in tension in a 3 point bending rig having a span of 10 cm (4 inches). It should be noted that the "3 point"

arrangement gives rise to more severe deformation stresses than does the 4 point bending mode, which in turn is best used when only "pure" bending stresses are required. In fact, the 3 point bend test resulted in a plastic hinge which greatly facilitated the controlled imposition of plastic strains to the aluminum substrate.

Two series of tests were carried out. In all tests the vertical displacement at the center of the specimen was measured with an extensometer set to a magnification ratio of 25; i.e., 1 mm of crosshead displacement corresponded to 25 mm of chart movement. This enabled the plastic deformation of the aluminum plate to be precisely measured. In the first series of tests, the coated plates were incrementally bent and the coating visually checked so that any cracking could be observed. The second series of tests were carried out in much the same manner except that the coatings were also monitored through acoustic emission (AE). It was thus possible to examine the coating integrity (adhesion problems or cracking behavior) in situ; and this significantly expediated the testing procedure.

RESULTS

Thermal Tests - non-destructive measurements

The heating-up curves of the aluminum plate are contrasted to those of the zirconia and alumina cermet coatings in Fig. 1. From these graphs it is obvious that:

(1) The heating-up rate at the periphery of the plate is less than those areas near the plate center;

(2) Thermocouples placed at corresponding positions on samples with different coatings exhibit different heating rates.

It was thus observed that, at temperatures less than approximately 500°C (for the center) and less than approximately 370°C (for the rim), the heating rate of the coated substrate was not substantially different from that of the bare

aluminum panel. However, when the center temperature was about 600°C and the rim about 500°C, the coatings exhibited a fire barrier effect, and would delay thermal failure of the coating-substrate combination.

The greatest influence on the heat flux pattern for both cermet coatings was approximately within the 20-50 Wt.% ceramic range. The center temperatures of the Al_2O_3 and ZrO_2 cermet coatings were similar, whereas the Al_2O_3 coatings exhibited a greater time to attain a 500°C rim temperature than did the corresponding ZrO_2 coatings.

One advantage of using a non-destructive test method is that many readings can be performed on one set of specimens. A summary of three consecutive heating cycles for the Al_2O_3 cermet (at the center position for temperatures of 400, 500 and 600°C) is shown in Fig. 2. It can be seen that the heating times to reach a set temperature increase with the number of heating cycles. In fact, for the 80% and 100% Al_2O_3 cermets, the coating exhibited a blister-type of defect which was generally followed by cracking of the coating. It is most likely that this effect is due to the severity of the test, where the heat input into a localized region is large when compared with the surrounding area. Therefore, stresses are set up between the cermet coating and the aluminum plate, with the consequence that cracking of the coating may expose the aluminum plate to more direct heat. The main point is that coating-substrate systems exhibit different thermal properties under thermal cycling conditions - however, the same trends are observed in any particular cycle.

The heating up rate data was normalized with respect to an uncoated aluminum substrate (Fig. 3). The dimensionless parameter is:-

$$\frac{\Delta T \text{ sample}}{\Delta T \text{ aluminum}} = \frac{\text{Temp. at Center (s) - Temp. at Rim (s)}}{\text{Temp. at Center (Al) - Temp. at Rim (Al)}}$$

Expression (1) compares the center and rim temperature of the cermet coated specimen to those of an aluminum plate relating to the heat flux between the center and rim of the sample. A relative value of "1" indicates that the thermal properties of the coated substrate do not differ substantially from those of the uncoated aluminum substrate. However, it is also important to know the absolute temperature of the sample. Therfore, the time-temperature profile for the centers of the sample are included in Fig. 3. In summary, the temperature difference ratio indicates the heat flow and distribution over the whole panel, whereas the absolute temperature shows when failure (by melting) may be imminent at the panel center.

Thermal Tests - destructive measurements

Coatings were also produced for destructive testing to establish the "burn through time" (Fig. 4). Failure was easily observed for the uncoated aluminum plates since the aluminum melted in the center and a molten pool sagged downwards. However, the failure point was not as easy to observe for the coated specimens, because the cermet coating obscured observation of the substrate. The failure in these cases was then taken as that point where the cermet coating glowed a distinct red color at the point of flame impingement - previous experience showed that beyond this time (about 10 to 15 sec) the aluminum panel melted catastrophically from the rear. However, in any case, a thermocouple was spring loaded to the center position and this was observed to reach temperatures in the vicinity of 650 to 660°C and also to move when the aluminum plate under it began to melt. Therefore, the accuracy of the "burn through" measurements is limited to about 5 to 10 seconds (the previous tests are accurate to approximately 5 seconds). The results show that the times for failure are a maximum at about 20% Al_2O_3 and 50% ZrO_2, and these correlate well with the previously described thermocouple measurements.

Mechanical Tests

It would normally be anticipated for the coatings to be subjected only to elastic loads during their service life; however, these tests were carried out to the plastic limit of the aluminum substrate, the deformation or failure of the coating (if any) then being examined.

The crosshead displacement vs force curves all exhibited a well defined "knee" at 6000 N (1350 lb.) which corresponded to the material behaving in a plastic hinge fashion (Fig. 5). The unloading curve allowed the permanent deflection of the aluminum plate to be calculated. The results of the first series of tests are shown in Table 2 (Specimens 1 to 4). It was also observed that the initial displacement tests show a large range which arises due to the difficulty of visually observing the occurrence of cracks. However, they all agree with the proposition that cracking occurred only after the elastic limit of the plate was reached.

The results of the second series of tests are also shown in Table 2 (Specimens 6 to 10). The typical shape of the AE vs time curve showed an increase upon loading due to initial contact of the 3 point bending supports on the specimen. The AE response then stabilized at a lower value (about 2.0 V) prior to increasing when the coating cracked (2.20 - 2.25 V). The results are reasonably consistent in predicting that coating failure will occur when the total displacement (elastic and plastic) of the specimen is greater than at least 2.7 mm.

DISCUSSION

It has been determined that cermet thermal barrier coatings can be used to increase the short-term life of aluminum plate when subjected to a "standard fire test". For zirconia coatings, the optimum ceramic content is 50 Wt.%, whereas it is about 20 Wt.% for equivalent performance from an alumina coating.

It can also be seen that more scope exists in the "fine tuning" of an optimum cermet composition. For example, it may be of benefit to use a cermet composition of low ceramic content in order to increase the overall adhesion of the deposit (and its resilience to bending stresses).

It would be expected that the thermal performance of the various coatings could be predicted by examining the thermal diffusivity and conductivity of the individual coatings. There is no such data available for flame sprayed coatings; however, the approximate measurements for the bulk materials at two temperatures are given in Table 3 [8], and values are also included for plasma-sprayed coatings [9]. Clearly both of these properties are a minimum for the bulk ZrO_2, and could be related to the thermal properties of sprayed coatings; although the incorporation of a metallic component would be an additional complication [10]. Also, it should be noted that the thermal properties of bulk ZrO_2 do not vary significantly with temperature when compared with alumina and, thus, its behavior over the entire temperature range should be more stable.

The graphs of relative temperature difference (Fig. 3) exhibit several trends. Values during the initial heating-up of the substrate (<40 sec) are generally greater than unity, and these reflect the insulating properties of the cermet coating such that the term {ΔT coating (center-rim)} is large. This large ΔT value arises even though the center temperatures of the coated and uncoated samples are comparable. Therefore, the cermet coating does not have the disadvantageous effect of concentrating the heat source - this effect, if it were observed, would lead to premature failure of the aluminum substrate.

The 40% ZrO_2 cermet coating does not behave appreciably different from the uncoated aluminum plate. However, the 50% ZrO_2 cermet coating shows far superior insulating properties (i.e., no heat conduction) and these are not further improved with higher ceramic compositions in the cermet. This property does

not necessarily indicate a better fire barrier since, in this case, the substrate takes 102 s to heat up to 500°C as compared to 109 s for the 60% ceramic coating. The optimal fire barrier cermet composition appears to lie between 50 and 60% ZrO_2, which correlates well with the destructive tests. There does not appear to be any progressive trend with changing composition and this is not unexpected. For example, it is not known how the relative volume fraction of two materials with different thermal conductivities effect the conduction path and whether equivalent spray parameters (as carried out in this study) reflect similar ceramic/metal particle interactions. Other factors which will change the thermal properties are the emissivity (or heat radiation properties) and the surface roughness (or real surface area) of the cermet coating.

The alumina coatings generally show a consistent decrease in the relative difference ratio during the progress of one thermal cycle (i.e., with an increase in temperature). Values less than unity arise because of the relative high conductivity of the alumina cermet coating, which then results in low temperature gradients over the substrate. The alumina coatings do not exhibit the high impedence to thermal conduction as exhibited by the 50% ZrO_2 coating; that is, the relative temperature difference is not consistently high over the whole temperature range. The 20% ceramic coating showed the greatest time to reach 500°C and also performed as the best fire barrier coating during destructive testing.

Another interesting aspect of the coating behavior has been their thermal cycling performance. The thermal barrier effect increases with the number of cycles, and this is suspected to arise from a change at the coating-substrate interface. In some cases, cracking was observed; and this phenomenon may reduce large scale cracking and increase the effective coating adhesion. On

the other hand, if blistering occurs, the events which lead to cracking are not controlled and, thus, coating adhesion to the substrate is poor. The interfacial blistering presents an interesting possibility of increasing the insulating qualities of the coating. Selective, partial peeling of the coating from the aluminum may be highly effective as a fire-barrier wall.

The results of the mechanical tests are straightforward. The major point is that the coatings adhere to the substrate beyond the elastic limit of the aluminum substrate. The onset of cracking was easily detected by acoustic techniques.

CONCLUSIONS

It was found that thermal-sprayed cermet coatings on aluminum retard melting and degradation of the base metal. The thermal behavior of the Al_2O_3 and ZrO_2 cermets was different and showed the best properties in the 20 and 50% (approximately) ceramic compositions respectively. There was no corrosion problem when the atomized Ni-Al was used. The cermet coatings adhered to the substrates under high plastic strains in excess of normal service conditions (assuming elastic criteria). A further investigation showed that acoustic emission techniques could readily detect coating detachment within the critical plastic deformation range of the aluminum substrate.

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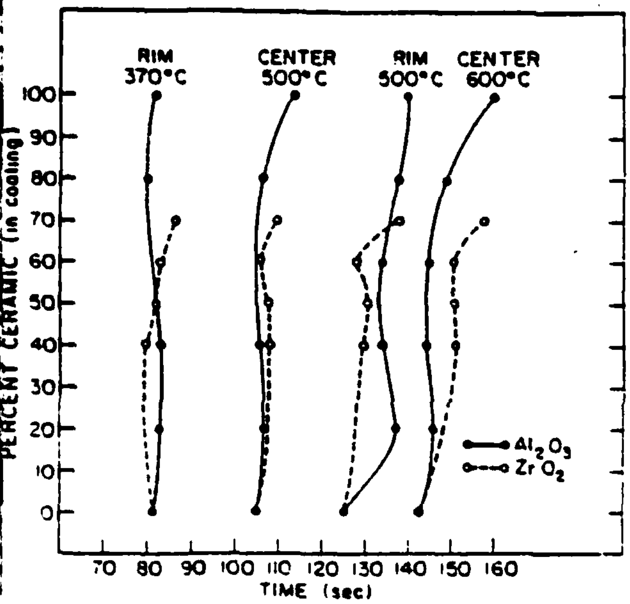

Fig. 1. Isothermal times of cermet coatings.

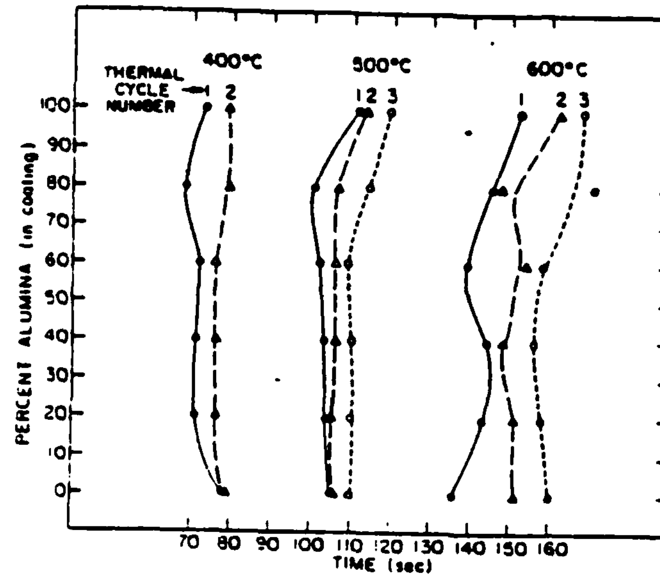

Fig. 2. Isothermal times of Al_2O_3 cermet coatings during 3 thermal cycles (no data exists at the 400°C isotherm of third cycle).

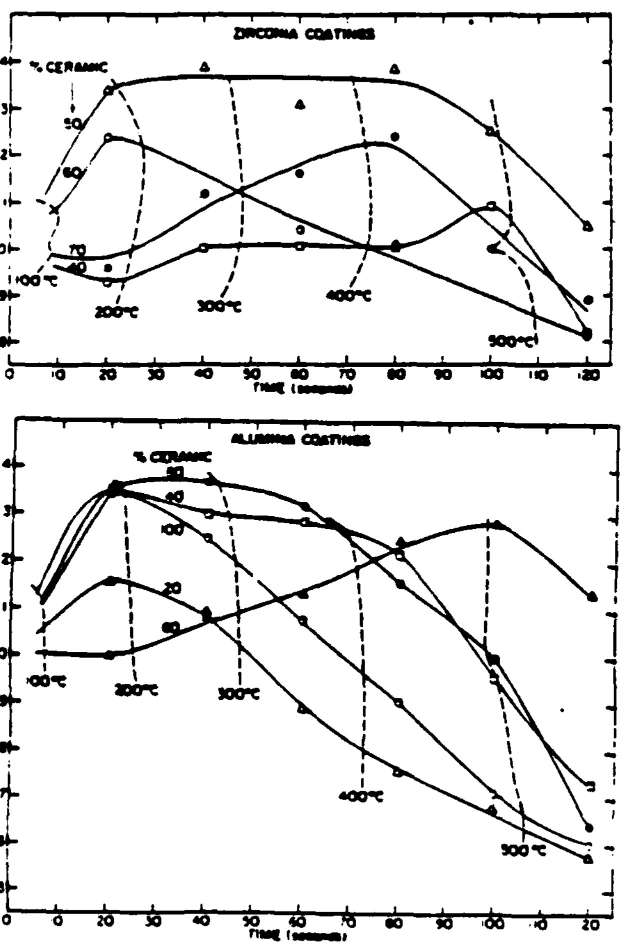

Fig. 3. Relative temperature difference of cermet coatings compared to aluminum plate. Isotherms are superimposed. (a) zirconia cermet coatings (b) alumina cermet coatings.

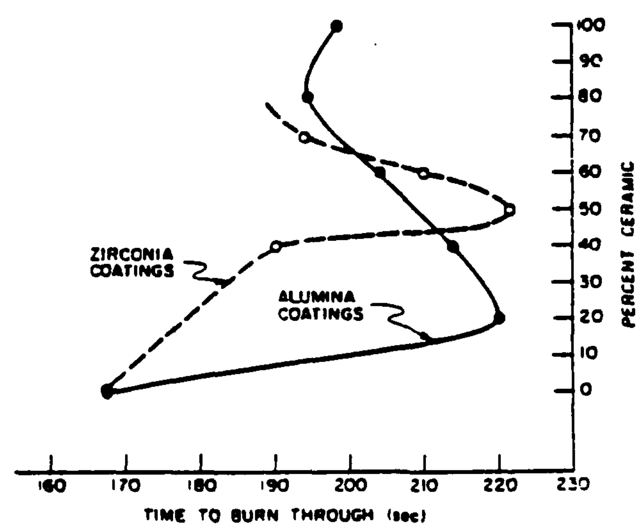

Fig. 4. Time to failure by "burn through" for cermet coatings.

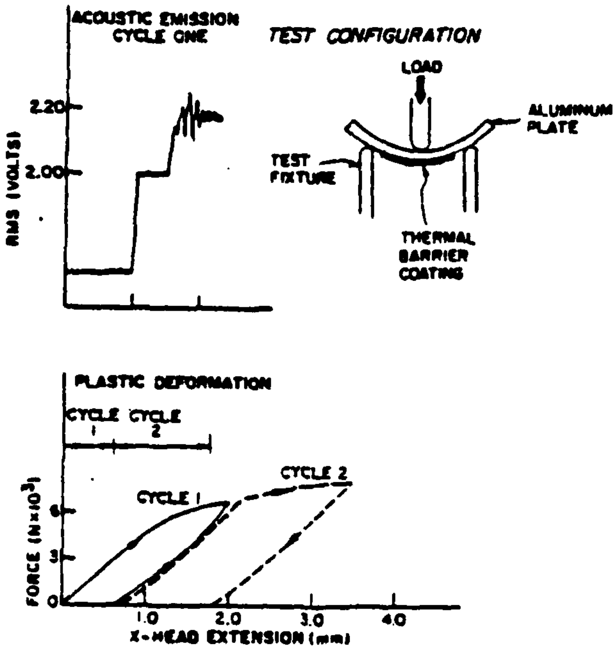

Fig. 5. Mechanical tests of coatings (a) test configuration (b) force vs extension curve for two loading cycles (c) acoustic emission response during the first loading cycle.

Table 1. Spray Parameters for Cermet Materials

Gun - 5P	
Nozzle - P7-G	
Metering Valve - No. 12	
Oxygen Pressure (MPa)	0.21
Oxygen Flow Rate*	34.0
Acetylene Pressure (MPa)	0.10
Acetylene Flow Rate*	34.0
Spray Distance (cm)	7.5-10
Spray Rate (Kg/h)**	1.8

*Units on Metco 2AF Flow meter.

**Powder vibrator used, no air jet used.

Table 2. Mechanical Properties of Coatings

Specimen Number and Loading Run	Weight % Ceramic	Accumulative Plastic Deformation (mm)	Cracking* Observation
1a	$20Al_2O_3$	< 9.0	extensive
2a	$40ZrO_2$	0.3	no
b		2.1	no
c		3.8	fine
3a	$50ZrO_2$	0.0	no
b		0.5	fine
4a	$50ZrO_2$	0.0	no
b		0.8	no
c		2.1	no
d		3.7	extensive
5a	$50ZrO_2$	0.0	
b		0.7	
c		1.7	yes after 1.7 mm
6a	$50ZrO_2$	0.3	
b		1.6	
c		3.7	
d		10.0	yes after 5.0 mm
7a	$50ZrO_2$	0.0	
b		0.6	
c		1.9	
d		4.1	yes after 4.1 mm
8a	$40ZrO_2$	0.0	
b		1.5	
c		1.5	
d		2.4	yes after 1.6 mm
9a	$20Al_2O_3$	0.7	
b		2.0	
c		4.2	yes after 2.9 mm
d		6.3	**
10a	$40Al_2O_3$	5.8	yes after 3.5 mm

(Runs 1-4 are visual observations).

*Runs 5-10 indicate the RMS voltage observations.

**RMS voltage changed after 1 mm of x-head displacement.

Table 3. Thermal Properties of Bulk and Plasma-Sprayed Materials (8,9)

	Thermal Diffusivity** $cm^2 sec^{-1}$		Conductivity** Watt $cm^{-1}K^{-1}$	
	300°K	900°K	300°K	900°K
ZrO_2	0.007	0.005	0.01	0.01
Al_2O_3	0.08	0.02	0.30	0.08
Al	0.90	0.70	2.5	1.0
Y_2O_3-ZrO_2*			0.03	0.07
NiCrAlY*			0.24	0.51

*Plasma-sprayed materials (exact formulations unknown).

**Data for comparison purposes only.

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